

phys. stat. sol. (b) **65**, 531 (1974)

Subject classification: 13.5.1

Institute of Physics, Odense University

Drift of Electron-Hole Drops in Exciton Density Gradients

By

I. BALSLEV and J. M. HVAM

The motion of electron-hole drops is analysed when nucleated in a non-uniform density of free excitons. The exciton condensation on the drop surface gives rise to a driving force towards regions with lower densities. This force and the internal friction of the exciton gas lead to a drift velocity which is proportional to the drop radius. In typical excitation geometries this motion is more important than drop diffusion, and the flight towards low density regions influences strongly the drop growth. It is pointed out that very large drops can be formed in a local minimum of the exciton density.

Es wird die Bewegung der Elektron-Loch-Tröpfchen in einem Exzitonengas mit inhomogener Dichte berechnet. Die Kondensation von Exzitonen auf der Tröpfchenoberfläche verursacht eine Kraft in Richtung niedrigen Exzitonendrucks. Diese Kraft und die Reibungskraft des Exzitonengases ergeben eine Geschwindigkeit, die dem Radius der Tröpfchen proportional ist. Es wurde gefunden, daß die entsprechende Bewegung in typischen Anregungsgeometrien viel wichtiger als die Diffusion ist und die Flucht nach Bereichen mit niedrigerer Dichte einen großen Einfluß auf das Wachsen der Tröpfchen hat. Sehr große Tröpfchen werden erwartet, wenn die Exzitonendichte ein lokales Minimum hat.

1. Introduction

At present the condensation phenomena of excitons at high densities in germanium are well understood from a number of independent experimental methods and theoretical considerations [1, 2], and a well defined phase diagram governing the transition from free excitons (FE) to electron-hole drops (EHD) is generally accepted. However, little is known about motion of EHD. The spatial distribution of the condensed phase as observed in luminescence experiments has until now been explained in terms of EHD diffusion [3 to 5], although the inferred diffusion coefficients are unexpectedly large and in mutual disagreement. Similar uncertainties concern the transport of EHD from the region of EHD formation to drop collecting p-n junctions.

In this paper we shall draw attention to the influence of supersaturation in the exciton generation region on the transport of EHD. It is obvious that FE diffusion from a small supersaturated region establishes FE densities above saturation in a much larger volume since the diffusion length of FE is of the order 1 mm. Thus, in a considerable part of this enlarged volume the formation of EHD takes place in an FE density gradient. Therefore we shall investigate the motion of EHD under such conditions and reveal a striking importance of the motion of drops due to the momentum transfer of condensing excitons.

2. Supersaturation and Diffusion of Free Excitons

In the interpretation of previous experiments [3, 4] it has been implicitly assumed that the formation of EHD is confined to the region of exciton generation, and that the existence of drops outside the region is due to drop transport. Here

we shall discuss some implications of these assumptions. Let n be the density of FE and n_0 its value at the point of saturation given by the phase diagram. Then $n - n_0$ expresses the degree of supersaturation in the FE gas. The overall density n^* of excitons in the condensed phase is proportional to NR^3 , where N is the density of EHD and R is the drop radius. In steady state $R \propto (n - n_0)$ (see Section 3) and consequently

$$n^* \propto N(n - n_0)^3. \quad (1)$$

In case of efficient drop nucleation $n - n_0 \ll n_0$ above the condensation threshold and n^* is proportional to excess excitation power. In the opposite extreme investigated by Pokrovskii [1] N is assumed constant (determined by the density of nucleation centres) and $n \gg n_0$ (large supersaturation) for excitation levels well above threshold. In this case

$$n^* \propto n^3. \quad (2)$$

Considering the excitation generation concentrated in a small volume (optical excitation) it is obvious that negligible supersaturation implies that EHD are not formed outside this volume since here the FE gas remains undersaturated. In the case of large supersaturation, on the other hand, the FE density may well exceed the saturation value at some distance from the exciton generation region due to FE diffusion. Hence, in the absence of drop transport, the density profiles of free and condensed excitons are coupled by (2), and in cw experiments the apparent diffusion length of EHD will be $L_{FE}/3$, where L_{FE} is the diffusion length of free excitons. Therefore the profile of the steady state luminescence from EHD [3, 5] is not directly related to the transport of EHD if the generation region is considerably supersaturated. Similar difficulties arise in the interpretation of pulsed experiments [4] since diffusion of FE during the excitation pulse and the time for n to decay below the saturation value n_0 may contribute to the spatial broadening of the EHD luminescence profile.

The above interpretational difficulties are present in all optical experiments (luminescence and Rayleigh scattering [6]) and give rise to the question whether the extension of the drop motion is substantially larger than the linear dimensions of the drops. However, the photovoltaic detection of EHD [7] is a clear evidence of considerable drop transport, since the FE density is zero in a collecting p-n junction due to dissociation of FE.

3. Equations of Motion of EHD in Non-Uniform FE Densities

In this section we shall evaluate the dynamics of EHD derived from the momentum transfer due to electron-hole recombination and exciton exchange through the drop surface. We include the presence of an FE density gradient ∇n which contribute to the drift since the condensation supplies the drops with excess momentum in the opposite direction of ∇n . For simplicity we neglect all other forces than those derived from the above mentioned momentum transfer. We further assume that the mean free path of FE is much larger than R which implies that condensing excitons are in thermal equilibrium with the lattice.

Let m and $\langle v \rangle$ be mass and thermal velocity of FE, respectively, and let V be the velocity of the drop considered. Denoting the life time and density in the condensed phase by τ_c and n_c , respectively, the drop mass M is expressed by

$$M = \frac{4}{3} \pi R^3 n_c m. \quad (3)$$

The growth rate of the drop is given by

$$\frac{1}{m} \frac{dM}{dt} = \pi R^2 \langle v \rangle (n - n_0) - \frac{4}{3} \pi R^3 \frac{n_c}{\tau_c}. \quad (4)$$

The change of momentum due to condensation is calculated to be

$$\left(\frac{d\mathbf{p}}{dt} \right)^+ = -\frac{2}{9} \pi R^3 m \langle v^2 \rangle \nabla n - \pi R^2 m \langle v \rangle \mathbf{V} n, \quad (5)$$

where $\langle v^2 \rangle$ is the mean square of the thermal velocity of FE to be approximated, for simplicity, by $\langle v \rangle^2$.

Since the velocity distribution of evaporating excitons is isotropic in the frame of the drop, each evaporating exciton removes the momentum $m\mathbf{V}$ from the drop. When calculating the momentum transfer due to recombination we assume that the phonon participation removes the correlation between the momenta of the electron and hole involved. Consequently, the recombining particles are randomly chosen, and the average crystal momentum transferred to the lattice is $m\mathbf{V}$ per recombining pair. The momentum change $(d\mathbf{p}/dt)^-$ due to evaporation and recombination is then given by

$$\left(\frac{d\mathbf{p}}{dt} \right)^- = -\left(\pi R^2 n_0 \langle v \rangle + \frac{4}{3} \pi R^3 \frac{n_c}{\tau_c} \right) m \mathbf{V}. \quad (6)$$

Furthermore

$$\frac{d\mathbf{p}}{dt} = \left(\frac{d\mathbf{p}}{dt} \right)^+ + \left(\frac{d\mathbf{p}}{dt} \right)^- = M \frac{d\mathbf{V}}{dt} + \mathbf{V} \frac{dM}{dt}. \quad (7)$$

Combining (3) to (7) we obtain

$$\frac{d\mathbf{V}}{dt} = -\frac{\langle v \rangle^2}{6n_c} \nabla n - \frac{3n \langle v \rangle}{2Rn_c} \mathbf{V} \quad (8)$$

and

$$\frac{dR}{dt} = \frac{n - n_0}{4n_c} \langle v \rangle - \frac{R}{3\tau_c}. \quad (9)$$

The absence of n_0 and τ_c in (8) indicates that only condensation processes contribute to the acceleration as implicitly assumed in (6).

The last term in (8) is a frictive force which transforms into Stoke's law for radii larger than the mean free path of FE. This friction defines a velocity relaxation time

$$\tau_v = \frac{2Rn_c}{3n \langle v \rangle} \quad (10)$$

and a mobility $\mu = \tau_v/M$. Using Einstein's relation we are able to assign to the random walk the diffusion coefficient

$$D_{\text{EHD}} = \frac{\tau_v kT}{M} \approx \frac{\langle v \rangle}{6\pi R^2 n}. \quad (11)$$

In steady state (8) defines a drift velocity

$$\mathbf{V}_d = -\frac{R \langle v \rangle \nabla n}{9n}, \quad (12)$$

which has physical meaning if the quantities determining it change little during the relaxation time τ_v . (9) defines a steady state radius

$$R_0 = \frac{3\tau_c (n - n_0) \langle v \rangle}{4n_c}. \quad (13)$$

The relaxation time for the change of R towards R_0 is $3\tau_c$ during which $n - n_0$ of the FE gas surrounding the drop must change little for obtaining $R \approx R_0$.

4. Motion of Drops in Typical FE Density Profiles

We shall discuss the motion of drops and the simultaneous change of their size given by (8) and (9) using parameters typical for Ge at 2K: $n_0/n_c \approx 10^{-4}$ [8], $n_c = 2 \times 10^{17} \text{ cm}^{-3}$, $\langle v \rangle = 10^6 \text{ cm/s}$ and $\tau_c = 50 \mu\text{s}$ [1, 2]. With these values we have performed a numerical integration of (8) and (9) for the drop motion in an appropriate one-dimensional FE density profile with $n_{\text{max}} \approx 2n_0$. In Fig. 1 are shown calculated trajectories for the spatial variation of R for drops nucleated with negligible radius and zero velocity at different positions in the supersaturated region. Inserting in (10) to (12) the typical parameters $n \approx n_0$, $\nabla n/n = 10 \text{ cm}^{-1}$ (a reciprocal FE diffusion length) and $R \approx 10^{-3} \text{ cm}$ we obtain $\tau_v = 6 \mu\text{s}$, $D_{\text{EHD}} = 0.003 \text{ cm}^2/\text{s}$ and $V_d = 10^3 \text{ cm/s}$.

From this analysis the most important conclusions are the following:

1. The velocities obtained from the numerical integration indicate an efficient relaxation towards the drift velocity V_d of (12). In the relevant parts of the motion V deviates less than 2% from V_d . This can be explained from a detailed analysis of (8) to (9) giving the simple result that the relative change rate of R , $d \ln R/dt$, is smaller than $(6\tau_v)^{-1}$ if $n > \frac{1}{2}n_0$ and $\tau_c > \tau_v$. Thus V_d changes less than 17% within a velocity relaxation time τ_v under these conditions and if $\nabla n/n$ is assumed constant.
2. The velocities are too high for a noticeable relaxation towards the steady state radius R_0 . Consequently, drops are ejected into the undersaturated region with a considerable size (see Fig. 1).
3. The drops must be nucleated extremely close to the FE density maximum to be able to attain radii comparable to the maximum steady state radius.
4. The time from nucleation to complete evaporation is of the order $300 \mu\text{s}$. The random walk found from the estimated diffusion coefficient (equation (11))

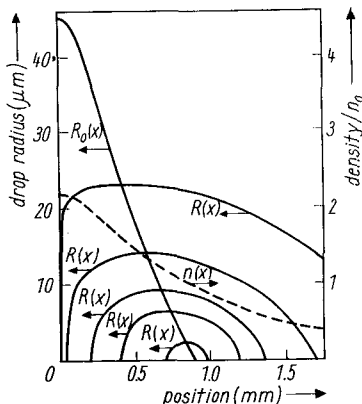


Fig. 1. Results of numerical integrations of equations (8) to (9) for a typical one dimensional free exciton density profile $n(x)$. The region with $x < 0.2 \text{ mm}$ is considered as the exciton generation region and characterized by a parabolic decay of $n(x)$ from $n_{\text{max}} = n(0) = 2.2n_0$. For $x = 0.2 \text{ mm}$ $n(x)$ equals $2n_0$ and decays exponentially with a decay length of 1 mm . This corresponds to an edge of the saturated region at $x \approx 0.9 \text{ mm}$. In the figure are shown the local steady state radius $R_0(x)$ and trajectories $R(x)$ for drops nucleated at different positions with zero velocity and radius. The trajectory with the largest maximum radius correspond to nucleation at $x = 0.001 \text{ mm}$. The parameters used in equations (8) to (9) are: $n_0/n_c = 10^{-4}$, $\tau_c = 50 \mu\text{s}$, and $\langle v \rangle = 10^6 \text{ cm/s}$

is negligible on this time scale. Therefore diffusion is of no importance in the motion of EHD except in regions with very small FE density gradients. At the point of maximum density the role of diffusion is to prevent excessive growth during "balancing" on the density maximum.

5. An analysis with linear density profiles in the region $0 < n < n_0$ (not shown) leads to trajectories which are essentially the same as for exponential profiles with equal slope at $n = n_0$. This last result is important in the interpretation of experiments on drop dissociation in a p-n junction which is an efficient drain for FE.

Approximate analytical solutions to equation (8) to (9) provide information on the influence of changing the parameters involved. Here we shall put $d\mathbf{r}/dt = \mathbf{V} = \mathbf{V}_d$ also in undersaturated regions. Then t can be eliminated from (8) to (9), and in one dimension we obtain

$$\frac{dR}{dx} \frac{dx}{dt} = -\frac{dR}{dx} \frac{dn}{dx} \frac{R\langle v \rangle}{9n} = \frac{n - n_0}{4n_c} \langle v \rangle - \frac{R}{3\tau_c}. \quad (14)$$

Let $n = n_0$ at $x = 0$ and $n = n_0 \exp(-x/L)$ with $L \gg R$. For negligible recombination and $|x| \lesssim L$ (14) has the solution

$$R(x) = (R_m^2 - (\alpha x)^2)^{1/2}, \quad (15)$$

where $\alpha = 3(n_0/n_c)^{1/2}/2$ and R_m is the maximum radius at $x = 0$. Thus the spatial range from "birth" to "death" of a drop is $2R_m/\alpha \approx 130R_m$ if $n_0/n_c = 10^{-4}$. The corresponding time is $9\pi L/(\alpha\langle v \rangle)$ independent of R_m . In case of considerable recombination it is convenient to introduce the length $\varrho = 3\tau_c\langle v \rangle n_0/4n_c$. Then, to first order in R/ϱ (15) should be changed into

$$R(x) = \left(R_m^2 - \frac{\alpha^2}{\varrho^2} (x + LR_m)^2 \right)^{1/2}, \quad (16)$$

where R_m is the maximum drop radius at $x = -LR_m/\varrho$. This solution agrees well with the trajectories in Fig. 1 for $R_m < 10^{-3}$ cm with the parameters $\varrho = 4 \times 10^{-3}$ cm and $\alpha = 0.015$. For a linear FE density profile with $dn/dx = -n_0/L$ it is relevant to express the radius of drops reaching the zero density point at $x = L$:

$$R(L) = \left(R_m^2 - \frac{L^2\alpha^2}{\varrho^2} (1 + R_m)^2 \right)^{1/2}. \quad (17)$$

For a given distribution of the maximum radius (17) can be used in estimating the size distribution of drops collected in p-n junctions. The general trend in such studies is that an increase of L (increased distance between generation region and junction) leads to an increase in typical size of collected drops and a decrease of the drop collection rate.

5. Experimental Consideration

Previous luminescence experiments are unable to verify clearly the above conclusions about the importance of drop drift in FE density gradients, since FE diffusion in a supersaturated region has the same effect on the EHD luminescence profile as drop drift, namely to broaden the profile of the overall density of the condensed phase beyond the region of exciton generation. A slight indication of drop drift in luminescence experiments might be the observed temperature dependence of the FE density profile at constant, high excitation level observed by Martin [5]. The half width increases noticeably at temperatures below 5 K which can be explained by FE transport via the process: condensa-

tion—drop drift—evaporation. Comparing the theory of the present paper with the Rayleigh scattering experiments [6] it is worth noting that the observed drop radii of 3 to 9 μm are in agreement with the numerical example in Fig. 1.

Dissociation of EHD in p-n junctions provides valuable information on the importance of drop drift. The observed size distribution as a function of distance between the excited region and the p-n junction¹⁾ agrees qualitatively with the prediction that large drops should be dominant for excitation far away from the junction. A diffusive theory would give the opposite result. The discrete size distribution of EHD observed recently [9] may be a consequence of the non-statistical nature of the drop motion in connection with very low density of nucleation centres.

There are several photovoltaic detection experiments suitable for a detailed study of the EHD motion mentioned here. Presently performed investigations²⁾ on charge distribution of collected drops concern the dependence on temperature, excitation level, bias and geometry. A very spectacular verification would be experiments in which a suitably arranged excitation on more than one surface of a Ge sample establishes a local FE density minimum at a level above saturation. In this case the present theory predicts very large drop radii which would otherwise be unattainable ($R_0 = 0.4 \text{ mm}$ for $n \approx 10n_0$).

6. Conclusion

We have proposed a transport mechanism of electron-hole drops which has classical origin and does not involve stress gradients, electric fields or scattering processes conventionally included in solid state physics. The important qualitative result is that diffusion of EHD is found negligible compared with the drift motion due to unavoidable FE density gradients. This motion is analogous to that of a particle with constant mass moving in a potential proportional to the density n and with a friction proportional to n/R . As drops are nucleated they grow and accelerate towards lower densities. Close to the edge of the supersaturated region the radius and velocity start decreasing and become zero at a range determined by the position of the nucleation centre. The model predicts that giant drops are formed if trapped in a three dimensional FE density minimum at a level well above saturation.

References

- [1] YA. POKROVSKII, *phys. stat. sol. (a)* **11**, 385 (1972).
C. BENOIT À LA GUILLAUME and M. VOOS, *Phys. Rev. B* **7**, 1723 (1973).
- [2] W. F. BRINKMAN and T. M. RICE, *Phys. Rev. B* **7**, 1508 (1973).
- [3] YA. POKROVSKII and K. I. SVISTUNOVA, *Fiz. tverd. Tela* **13**, 1485 (1971); *Soviet Phys. — Solid State* **13**, 1241 (1971).
- [4] C. BENOIT À LA GUILLAUME, M. VOOS, and F. SALVAN, *Phys. Rev. Letters* **27**, 1214 (1971).
- [5] R. W. MARTIN, *phys. stat. sol. (b)* **61**, 223 (1974).
- [6] YA. POKROVSKII and K. I. SVISTUNOVA, *Zh. eksper. teor. Fiz.* **13**, 297 (1971); *Soviet Phys. — J. exper. theor. Phys.* **13**, 212 (1971).
- [7] C. BENOIT À LA GUILLAUME, M. VOOS, F. SALVAN, J. M. LAURANT, and A. BONNOT, *C. R. Acad. Sci. (France)* **272 B**, 236 (1971).
- [8] T. K. LO, B. J. FELDMAN, and C. D. JEFFRIES, *Phys. Rev. Letters* **31**, 224 (1973).
- [9] J. M. HVAM and O. CHRISTENSEN, to be published.

(Received July 9, 1974)

¹⁾ Unpublished experimental results.

²⁾ Current experimental work at our laboratory.